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DESCRIPTION

RUBBER COMPOSITION CONTAINING MODIFIED CONJUGATED
DIENE-BASED POLYMER BONDED TO FULLERENE

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TECHNICAL FIELD

The present invention relates to a rubber composition containing a modified conjugated diene-based polymer having a bonded fullerene in the molecule thereof. More specifically, it relates to a rubber composition containing a modified diene-based polymer having an excellent processability, superior balance between the modulus and the heat buildup, excellent cold flowability and superior $\tan \delta$ balance with a low $\tan \delta$ value at 60°C and high $\tan \delta$ value at 0°C.

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BACKGROUND ART

A fullerene is a spherical compound consisting of only carbon atoms. The term includes higher order fullerenes consisting of 60 carbon atoms (C_{60}) and higher even numbers of carbon atoms. These include 12 five-member rings and 20 or more five-member rings, six-member rings or seven-member rings. It has been learned in recent years that the most representative C_{60} is a molecule extremely high in reactivity due to its special electron system. This reactivity is utilized for various types of chemical modification. Blending a spherical carbon molecule fullerene into a rubber component, as a filler, is described in, for example, Japanese Patent Publication (A) No. 10-168238. Further, polymerizing isoprene by living anion polymerization and modifying its terminals by a fullerene is described in, for example, *Macromolecules* 1997, 30, 2546-2555. However, it has not been known that the conjugated diene-based polymer synthesized by the method described in *Macromolecules* is useful as a rubber composition.

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DISCLOSURE OF THE INVENTION

The objects of the present invention are to provide

a rubber composition containing a modified conjugated diene-based copolymer obtained by chemically bonding a fullerene to a conjugated diene-based polymer and having superior physical properties, more particularly a rubber composition having superior processability, high modulus and superior balance of the modulus and the heat buildup as well as a rubber composition with an excellent cold flowability and a superior $\tan \delta$ balance of a low $\tan \delta$ value at 60°C and a high $\tan \delta$ value at 0°C.

In accordance with the present invention, there is provided a rubber composition comprising 100 parts by weight of a rubber component containing a modified conjugated diene-based polymer having fullerene bonded thereto in the molecule and a weight average molecular weight of 50,000 or more in an amount of 0.5 to 100% by weight based upon the total amount of the rubber component and 5 to 100 parts by weight of a reinforcing filler.

According to the present invention, as shown below, a rubber composition having excellent processability and modulus, superior balance of the modulus and the heat buildup, excellent cold flowability and superior $\tan \delta$ balance can be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be explained with reference to the following figures, in which

FIG. 1 is a graph showing the relationship between the $\tan \delta$ (60°C) and 300% modulus of Example 1 and Comparative Examples 1 to 4, and

FIG. 2 is a graph showing the relationships between the weight average molecular weight and $\tan \delta$ balance in the Example 2 and Comparative Examples 5 to 7.

BEST MODE FOR CARRYING OUT THE INVENTION

As explained above, a fullerene is a spherical compound consisting solely of carbon atoms and the term includes higher order fullerenes composed of 60 carbon

atoms (C_{60}) or higher even numbers of carbon atoms. These include 12 five-member rings and 20 or more five-member rings, six-member rings or seven-member rings. As typical examples, C_{60} , C_{70} , C_{76} , C_{78} , C_{82} , C_{84} , C_{90} , C_{96} , C_{120} , etc. may
5 be mentioned. It is known that the most representative C_{60} is a molecule extremely high in reactivity due to the special electron system thereof. This reactivity is utilized for various types of chemical modification. Further, due to the special electron system and large
10 size of the molecule, a polymer having a fullerene in the molecule thereof is expected to exhibit unique properties in terms of the electrical, magnetic, mechanical, and thermal characteristics thereof and is expected as a functional material.

15 The inventors found that, by synthesizing a conjugated diene-based polymer having a fullerene bonded to the molecule thereof and compounding it to a rubber composition, an excellent processability, high modulus, and superior balance of the modulus and the heat buildup
20 thereof are exhibited, further an excellent cold flowability is exhibited, and, when considered as a tread rubber for a tire, the $\tan \delta$ (60°C) value usable as an indicator of the rolling resistance is low, the $\tan \delta$ (0°C) value usable as an indicator of the wet skid
25 resistance is high, that is, the desired superior $\tan \delta$ balance is exhibited, and thereby completed the present invention.

The fullerene-modified conjugated diene-based polymer compounded in the rubber composition according to
30 the present invention has a weight average molecular weight of 50,000 or more, preferably 100,000 to 2,000,000, and constitutes 0.5 to 100% by weight, preferably 10 to 100% by weight, of the rubber ingredient compounded in the rubber composition. The amount of
35 modification by the fullerene is not particularly limited, but is preferably 0.001 to 2 molecules, more

preferably 0.01 to 2 molecules, per chain of the modified conjugated diene-based polymer.

5 If the weight average molecular weight of the fullerene-modified conjugated diene-based polymer is less than 50,000, it is not preferable because, since the molecular weight is too low, the effect obtained by the modification is cancelled out. If the compounding amount
10 the fullerene-modified conjugated diene-based polymer in the rubber component compounded into the rubber composition of the present invention is too small, it is not preferable because the desired physical properties cannot be obtained.

The modified conjugated diene-based polymer having a fullerene in the molecule, which is compounded into the
15 rubber composition according to the present invention, can be synthesized, for example, by reacting the growing terminal anions of the conjugated diene-based polymer formed by anion polymerization and the fullerene. Examples of such synthesized polymer are those
20 synthesized by reacting the growing terminal anions of a copolymer obtained by an anion polymerization of an aromatic vinyl monomer and a conjugated diene monomer, as a conjugated diene-based polymer, and a fullerene. Examples of such an aromatic vinyl monomer, are styrene,
25 α -methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2,4-diisopropylstyrene, 2,4-dimethylstyrene, 4-t-butylstyrene, etc. Among these, styrene is preferable. Examples of the conjugated diene monomer, are 1,3-butadiene, 2,3-dimethyl-1,3-butadiene,
30 1,3-pentadiene, 2-methyl-1,3-butadiene (i.e., isoprene), etc. Among these, 1,3-butadiene and isoprene is preferable. Further, the modified conjugated diene-based polymer having the aromatic vinyl monomer content of 10 to 80% by weight, more preferably 10 to 50% by weight, is
35 preferable for maintaining a suitable glass transition temperature. Such a modified conjugated diene-based polymer is obtained, for example, by copolymerizing

styrene, as an aromatic vinyl monomer, and butadiene, as a conjugated diene monomer to form a styrene-butadiene copolymer rubber (SBR) and further, by reacting the growing terminal anions of the copolymer and fullerene, to form a fullerene-modified styrene-butadiene copolymer rubber. Further, as other conjugated diene-based polymers, various types of diene-based polymers such as polyisoprene rubber (IR), various types of polybutadiene rubber (BR), styrene-isoprene copolymer rubber, styrene-butadiene-isoprene copolymer rubber, may be used. A modified conjugated diene-based polymer, when polymerizing such a conjugated diene-based polymer, as shown also in the Synthesis Example explained below, can be produced by adding a commercially available fullerene to modify the polymer at the time of completion of polymerization.

As other rubber ingredient compounded into the rubber composition according to the present invention, any diene-based rubber or rubber other than a diene-based rubber usable in a rubber composition can be mentioned. As a representative diene-based rubber, various types of natural rubber (NR), various types of polyisoprene rubber (IR), various types of polybutadiene rubber (BR), various types of styrene-butadiene copolymer rubber (SBR), various types of ethylene-propylene-diene three-way copolymer rubber (EPDM), various types of chloroprene rubber, various types of butyl rubber, various types of halogenated butyl rubber, various types of acrylonitrile-butadiene copolymer rubber etc. may be mentioned. Further, as the non-diene-based rubber, various types of ethylene-propylene copolymer rubber, various types of ethylene-butene copolymer rubber, various types of brominated isobutylene-paramethylstyrene copolymer rubber, various types of epichlorohydrin rubber, various types of silicone rubber, etc. may be mentioned. These may be used alone or in any mixture thereof.

The rubber composition according to the present

invention may optionally includes a reinforcing filler and, another compounding agent. As the reinforcing filler, carbon black, silica, etc. is preferably compounded. The compounding amount of the reinforcing
5 filler is not particularly limited, but preferably 5 to 100 parts by weight, more preferably 10 to 90 parts by weight, based upon 100 parts by weight of the rubber component. As the carbon black capable of compounding into the rubber composition according to the present
10 invention, carbon black usable in a rubber composition such as furnace black, acetylene black, thermal black, channel black, graphite, any may be mentioned. As the silica usable in the rubber composition according to the present invention, any silica capable of compounding into
15 a rubber composition may be mentioned.

The rubber composition according to the present invention contains preferably 0.1 to 10 parts by weight, more preferably 0.2 to 7 parts by weight, of a
vulcanization agent, based upon 100 parts by weight of
20 the rubber component. In addition, the rubber composition according to the present invention may contain a vulcanization or cross-linking accelerator, various types of oil, an antioxidant, a plasticizer, or other various types of additives generally compounded for rubber use.
25 This formulation may be mixed and vulcanized by a general method to form a composition used for vulcanization or cross-linking. The compounding amounts of these additives may be made any conventional general amounts of compounding, unless the object of the present invention
30 is not adversely affected. The rubber composition according to the present invention is useful as a rubber composition for a tire tread, where a superior balance of modulus and heat buildup and a superior $\tan \delta$ balance are required. In addition, for example, use for belts, hoses,
35 rubber shock absorbers, rollers, sheets, linings, rubberized cloth, seal materials, gloves, fenders, and various types of pharmaceutical and physicochemical

products, civil engineering products, and rubber products for maritime use, automobiles, railroads, office automation, aircraft, packaging, etc. is possible.

EXAMPLES

5 Examples of the present invention will now be explained, but the present invention is by no means limited to the following Examples.

Example 1 and Comparative Examples 1 to 4

10 In each formulation shown in Table I (parts by weight), the components other than the vulcanization accelerator and sulfur were mixed by a 0.25 liter internal mixer for 3 to 5 minutes to obtain a master batch, which was then mixed with the vulcanization
15 accelerator and sulfur by an 8-inch open roll to obtain a rubber composition. This composition was press vulcanized in a 15x15x0.2 cm mold at 160°C for 20 minutes to obtain a rubber sheet.

 Each vulcanized rubber sheet obtained above was evaluated by the following method.

20 300% modulus (MPa): Measured according to JIS K6301.

 tan δ (60°C): Value measured using viscoelasticity spectrometer (Toyo Seiki) at a temperature of 60°C under conditions of an initial strain of 10%, a dynamic strain of $\pm 2\%$, and a frequency of 20Hz. Note that when
25 considering tread rubber for a tire, the lower this value, the smaller the rolling resistance and therefore the smaller the heat buildup and the smaller the fuel consumption.

 Processability at discharge: State at time of
30 discharge after mixing judged visually.

G: Good

F: Fair

P: Poor

Table I

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Ex. 1
<u>Formulation</u> (parts by weight)					
IR-A ¹⁾	100	-	-	-	-
IR-B ²⁾	-	100	-	-	-
IR-C ³⁾	-	-	100	-	-
IR-D ⁴⁾	-	-	-	100	-
IR-FUL ⁵⁾	-	-	-	-	100
Carbon black ⁶⁾	50	50	50	50	50
Zinc oxide ⁷⁾	3	3	3	3	3
Stearic acid ⁸⁾	2	2	2	2	2
Antioxidant ⁹⁾	1	1	1	1	1
Vulcanization accelerator NS ¹⁰⁾	1	1	1	1	1
Sulfur ¹¹⁾	2	2	2	2	2
<u>Evaluated physical properties</u>					
300% modulus (MPa)	13.8	13.9	14.1	13.4	15.4
tan δ (60°C)	0.1499	0.1076	0.1210	0.1358	0.1173
Processability upon discharge	G	P	P	F	G

1) to 4) Unmodified polyisoprene (see Synthesis Example)

5) Fullerene-modified polyisoprene (see Synthesis Example)

6) Shoblack N339 (Showa Cabot)

7) Zinc White No. 3 (Seido Chemical)

8) Beads Stearic Acid (Kiri, NOF Corporation)

9) Santoflex 13 (6C, Monsanto Japan)

10) Noccelar NS-P (Ouchi Shinko Chemical Industrial)

11) Oil-extended sulfur (Karuizawa Refinery)

Synthesis Example

The unmodified polyisoprenes IR-A, IR-B, IR-C and IR-D and the modified polyisoprene IR-FUL used were synthesized as follows. The chemical reagents used for the synthesis were as follows.

Cyclohexane and isoprene: Made by Kanto Chemical, dehydrated by Molecular Sieve 4A, and bubbled with

nitrogen.

n-Butyl lithium: Made by Kanto Chemical, n-hexane solution 1.6 mol/liter.

5 Toluene: Made by Kanto Chemical, refluxed in the presence of sodium for about 1 week, checked for deep blue color of benzophenone ketyl (i.e., indicator of dehydration), then distilled.

Fullerene: Tokyo Kasei C₆₀>99.9% fullerene degassed and dried.

10 Synthesis of Unmodified IR-A to IR-D

A nitrogen-substituted 10-liter autoclave reactor was charged with 2830 g of cyclohexane and 517.6 g (7.598 mol) of isoprene, and then stirring started. After the temperature of the content in the reaction vessel reached 15 50°C, 1.854 ml (2.911 mmol) of n-butyl lithium was added. After the polymerization conversion rate reached 100%, 0.5 ml of methanol was added and the resultant mixture stirred for 10 minutes. The polymer solution thus obtained was given a small amount of an antioxidant 20 (Irganox 1520) and concentrated in vacuo to remove the solvent. The polymer was coagulated in methanol, washed, then dried to obtain polyisoprene. The addition amounts of n-butyl lithium were changed to produce IR-A to IR-D.

25 The number average molecular weight M_n of the unmodified polyisoprene obtained above was measured by gel permeation chromatography (GPC). The results were as follows:

	IR-A:	325,000
	IR-B:	941,000
30	IR-C:	837,000
	IR-D:	513,000

Synthesis of Fullerene-Modified IR (IR-FUL)

35 A nitrogen-substituted 10-liter autoclave reactor was charged with 2272 g of cyclohexane and 204.3 g (2.999 mol) of isoprene, and then stirring started. After the temperature of the content in the reaction vessel reached 50°C, 1.481 ml (2.311 mmol) of n-butyl lithium was added.

After the polymerization conversion rate reached 100%, 11.23 g (0.02885 mmol) of a fullerene (C_{60}) in a 0.185% by weight toluene solution was added and the resultant mixture stirred for 1 hour. Next, 0.5 ml of methanol was added and the resultant mixture stirred for 1 hour. The polymer solution thus obtained was given a small amount of an antioxidant (Irganox 1520) and the resultant mixture was concentrated in vacuo to remove the solvent. The polymer was coagulated in methanol, washed, then dried to obtain a fullerene-modified polyisoprene. The number average molecular weight M_n was 859000, the result of measurement of the weight average molecular weight M_w by gel permeation chromatography (GPC) was 1202000, and the M_w/M_n was 1.40.

Table I shows the results of the evaluation. Further, FIG. 1 shows the relationship between the modulus and the $\tan \delta$ at 60°C. In FIG. 1, points A to D show Comparative Examples 1 to 4, while IR-FUL shows Example 1.

Example 2 and Comparative Examples 5 to 7

In each formulation shown in Table II (parts by weight), the components other than the vulcanization accelerator and sulfur were mixed in a 0.25 liter internal mixer for 3 to 5 minutes to obtain a master batch, which was then mixed with the vulcanization accelerator and sulfur by an 8-inch open roll to obtain a rubber composition. This composition was press vulcanized in a 15x15x0.2 cm mold at 160°C for 20 minutes to obtain a rubber sheet.

Each vulcanized rubber sheet obtained above was evaluated by the following method.

Viscoelasticity: $\tan \delta$ (60°C) and $\tan \delta$ (0°C) values measured using a viscoelasticity spectrometer (Toyo Seiki) at temperatures of 60°C and 0°C under conditions of an initial strain of 10%, a dynamic strain of $\pm 2\%$ and a frequency of 20Hz and the ratio of the same.

Note that the lower the value of the $\tan \delta$ (60°C), the smaller the rolling resistance, therefore the smaller the heat buildup and the smaller the fuel consumption, while the higher the value of the $\tan \delta$ (0°C), the larger the wet skid resistance and the better the braking performance on a wet road surface.

Cold flowability: Existence of any change in shape of unvulcanized rubber sheet after allowing to stand for 24 hours was visually observed.

Table II

	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Ex. 2
Formulation (parts by weight)				
SBR-A ¹⁾ M _w 478000 ¹²⁾ St: 22.1% by weight, Vinyl: 58.5% ¹³⁾	100	-	-	-
SBR-B ²⁾ M _w 643000 ¹²⁾ St: 22.0% by weight, Vinyl: 59.9% ¹³⁾	-	100	-	-
SBR-NF ³⁾ M _w 403000 ¹²⁾ St: 19.9% by weight, Vinyl: 59.9% ¹³⁾	-	-	100	-
SBR-FCP ⁴⁾ M _w 769000 ¹²⁾ St: 26.0% by weight, Vinyl: 61.3% ¹³⁾	-	-	-	100
Carbon black ⁵⁾	60	60	60	60
Zinc oxide ⁶⁾	3	3	3	3
Stearic acid ⁷⁾	1	1	1	1
Antioxidant ⁸⁾	1	1	1	1
Aromatic oil ⁹⁾	5	5	5	5
Vulcanization accelerator CZ ¹⁰⁾	2	2	2	2
Sulfur ¹¹⁾	2	2	2	2
Viscoelasticity				
$\tan \delta$ (60°C)	0.201	0.204	0.277	0.187
$\tan \delta$ (0°C)	0.679	0.675	0.929	1.091
$\tan \delta$ (0°C)/ $\tan \delta$ (60°C)	3.378	3.309	3.354	5.834
Cold flow				
24 hours	Yes	Yes	Yes	No

1) Nipol NS120 (Nippon Zeon)

2) JSR SL563 (JSR)

3) Unmodified SBR (see Synthesis Example)

4) Fullerene-modified SBR (see Synthesis Example)

5) Shoblack N339 (Showa Cabot)

- 6) Zinc White No. 3 (Seido Chemical)
- 7) Beads Stearic Acid Kiri (NOF Corporation)
- 8) Santoflex 13, 6C (Monsanto Japan)
- 9) Extract No. 4S (Shell Japan)
- 5 10) Noccelar CZ-G (Ouchi Shinko Chemical Industrial)
- 11) Oil-extended sulfur (Karuizawa Refinery)
- 12) Weight average molecular weight
- 13) St: Amount of styrene, Vinyl: Amount of vinyl

10 Synthesis Example

Note that the reagents used in the following
Synthesis Examples were as follows:

15 Cyclohexane, Styrene: Made by Kanto Chemical,
dehydrated by Molecular Sieve 4A, and bubbled with
nitrogen.

Butadiene: Made by Japan Petrochemical, purity
99.3%, dehydrated by Molecular Sieve 4A.

n-Butyl lithium: Made by Kanto Chemical, n-hexane
solution 1.58 mol/liter.

20 N,N,N',N'-Tetramethylethyl diamine (TMEDA):
Dehydrated by Molecular Sieve 4A and bubbled with
nitrogen.

Toluene: Made by Kanto Chemical, refluxed in the
presence of metal sodium for about 1 week, checked for
25 deep blue color of benzophenoneketyl (i.e., indicator of
dehydration), then distilled.

Fullerene: Tokyo Kasei C₆₀>99.9% fullerene dehydrated
and dried.

Synthesis of Unmodified SBR (SBR-NF)

30 A nitrogen-substituted 10-liter autoclave reactor
was charged with 3138 g of cyclohexane, 115.6 g (1.110
mol) of styrene, 438.9 g of butadiene (8.172 mol) and
1.102 ml (7.398 mmol) of TMEDA and then stirring started.
After the temperature of the content in the reaction
35 vessel reached 50°C, n-butyl lithium was added in an
amount of 3.805 ml (5.936 mmol). After the polymerization
conversion rate reached 100%, 0.5 ml of methanol was

added and the resultant mixture stirred for 30 minutes. The polymer solution obtained was given a small amount of an antioxidant (Irganox 1520) and concentrated in vacuo to remove the solvent. The polymer was coagulated in methanol, washed, then dried to obtain a solid polymer. The amount of styrene of the polymer thus obtained was 19.9% by weight (measured at $^1\text{H-NMR}$), the amount of vinyl was 59.9% (measured at $^1\text{H-NMR}$), and the weight average molecular weight (M_w) was 403000 (measured by the above-mentioned method).

Synthesis of Fullerene-Modified SBR (SBR-FCP)

A nitrogen-substituted 10-liter autoclave reactor was charged with 3137 g of cyclohexane, 113.8 g (1.093 mol) of styrene, 438.9 g (8.172 mol) of butadiene, and 0.812 ml (5.535 mmol) of TMEDA and stirring started. After the temperature of the content in the reaction vessel reached 50°C, 3.330 ml (5.266 mmol) of n-butyl lithium was added. After the polymerization conversion rate reached 100%, 49.30 g (0.4588 mmol) of a fullerene (C_{60}) in a 0.670% by weight toluene solution was added and the resultant mixture stirred for 2 hours. Next, 0.5 ml of methanol was added and the resultant mixture stirred for 1 hour. The polymer solution obtained above was given a small amount of an antioxidant (Irganox 1520) and concentrated in vacuo to remove the solvent. The polymer was coagulated in methanol, washed, then dried to obtain a solid polymer. The styrene content of the polymer obtained was 26.0% by weight, the amount of vinyl was 61.3% and the weight average molecular weight (M_w) was 769000 (measured by the above-mentioned methods).

In each formulation shown in Table II (parts by weight), the components other than the vulcanization accelerator and sulfur were mixed in a 0.6 liter internal mixer for 3 to 5 minutes to obtain a master batch which was mixed with the vulcanization accelerator and sulfur by an 8-inch open roll to obtain a rubber composition. This composition was press vulcanized in a 15x15x0.2 cm

mold at 160°C for 20 minutes to obtain a rubber sheet.

Table II shows the results of the evaluation.

Further, FIG. 2 shows the relationship between the weight
average molecular weight and the $\tan \delta$ (0°C)/ $\tan \delta$ (60°C)
5 ratio. In FIG. 2, the points A, B and NF show Comparative
Examples 5 to 7, while the point FCP shows Example 2.

INDUSTRIAL APPLICABILITY

As explained above, the rubber composition according
to the present invention is excellent in the
10 processability, high in the modulus, superior in balance
of the modulus and the heat buildup, and excellent in the
cold flowability and is superior in the $\tan \delta$ balance
(that is, low in $\tan \delta$ (60°C) and high in $\tan \delta$ (0°C)),
and therefore, is suitable for use, for example, as a
15 rubber for a tire tread, etc.